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Constitutive analysis of the nonlinear viscoelastic properties of cellulosic fiber gels produced from corn or oat hulls☆

C.J. Carriere*, G.E. Inglett

United States Department of Agriculture, Cereal Products and Food Science Research Unit, Biomaterials Processing Research Unit, National Center for Agricultural Utilization Research, Agricultural Research Service, 1815 North University Street, Peoria IL 61604, USA

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Abstract

The evaluation and development of validated models for the nonlinear viscoelastic (VE) behavior of materials is an important area of research, which has impact on a number of industrial processes including those in the food industry. Various nonlinear VE models have been developed over the years and evaluated for petroleum-based polymers, however, our understanding of the nonlinear VE behavior of biopolymers of industrial import lags our understanding of synthetic polymers. In the work reported herein, the nonlinear VE behavior of several cellulosic fiber gels prepared from either corn or oat hulls were investigated. The rheological properties were measured using a Rheometrics Series IV controlled-strain rheometer equipped with a cone and plate fixture. The measurements were conducted at 23 ± 0.1 °C. The rheological data were interpreted using a strain separable K-BKZ type (Wagner) model with a damping function evaluated from stress relaxation data. The Wagner model was found to provide an accurate description of the rheological behavior of the suspensions.
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Keywords: Rheology; Constitutive analysis; Flour; Nonlinear viscoelasticity

1. Introduction

Over the past several years, considerable research efforts have been directed towards understanding the nonlinear viscoelastic (VE) behavior of materials. The investigation of nonlinear VE properties in materials presents a rich field of study. Nonlinear VE properties are of import in a number of diverse industrial processes including extrusion, injection molding, steam-injection cooking, dough mixing, and film tentering. Nonlinear VE properties may be observed in many materials at high strains, however, the effect can also be observed at small strains for many systems such as suspensions, and composites. (Matsumoto, Hitomi, & Onogi, 1975; Russel, 1980; Russel, Saville, & Schowalter, 1989; Simhambhatla & Leonov, 1995; Watanabe et al., 1996, 1997). In many of these systems the suspended particles form aggregates which exhibit highly nonlinear VE behavior even at low strains. (Russel, 1980; Russel et al., 1989; Matsumoto et al., 1975).

Nonlinear VE behavior is also observed in a number of biological and food systems. (Lapasin & Pricl, 1995; Lapasin, Pricl, & Tracanneli, 1992). Many biological polymers form weak physical gels which display nonlinear VE properties similar to those observed in many synthetic polymer concentrated solutions and melts at high strains, or polydisperse systems at low strains. (Lapasin & Pricl, 1995; Lapasin et al., 1992). For many biological polymer systems, associations between the various components of a blend, or between the biopolymer and the solvent, can lead to unexpected nonlinear VE behavior such as multiple stress overshoots during the start up of steady-state shear, or regions of shear-thickening behavior. The characterization and understanding of these phenomena in biopolymer systems severely lags our understanding of nonlinear VE behavior in synthetic polymers.

In the work reported herein, the nonlinear VE behavior of cellulosic fiber gels produced from either corn or oat hulls

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* Corresponding author. Tel.: +1-309-681-6551; fax: +1-309-681-6685.
E-mail address: carriecj@ncaur.usda.gov (C.J. Carriere).

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were characterized. The responses of the gel suspensions were examined under various steady-state and transient rheological deformations. The behavior of the suspensions were characterized using a time-strain separable Wagner model with a Soskey-Winter damping function.

2. Experimental

2.1. Materials

Corn hulls, called corn bran, were obtained from ConAgra Corn Processing (Atchison, KS). The corn bran was a distribution of finely ground hulls obtained from the dry milling of corn with over 90% passing through a US number 60 sieve. Another source of corn hulls, called wet-milled corn hulls, was obtained from Cargill (formerly Cerestar, Hammond, IN). After the hulls were removed from wet process stream, they were air-dried and ground to a particle size of less than about 1 mm. Taka-Therm L-340™ was supplied by Genencor International (formerly, Solvay Enzymes, Elkhart, IN). Taka-Therm L-340™ is a thermostable α-amylase referred to as 1,4-α-*d*-glucan glucanohydrolases. It has the essential enzymatic characteristics of those produced by the Bacillus stearothermophilus strains. Oat hulls were obtained from ConAgra Oat Processing (Nebraska). The oat husks were finely ground to less than 1 mm. Proximate analyses for moisture, protein, ash, and lipid were obtained by the official procedures of AACC (1983) and for total dietary fiber by AOAC (1990).

2.2. Preparation of cellulosic fiber gels

2.2.1. Corn cellulosic gel preparation

In a 20 l plastic tank, 1 kg of fine ground corn hulls was mixed with 11 l of water for the first stage treatment. Approximately 10 g of a 50% sodium hydroxide solution (sp. gr. 1.52; 13.3% alkali concentration) was added to adjust the pH to about 6.8. After heating the slurry to 90–94 °C, 2.4 ml of Taka-Therm L-340™ was added to the mixture, giving a concentration of 204 MWU/g substrate. The mixture was sheared in a Premier Model 90 Dispersator™ (Premier Mill Corporation, Reading, MA) equipped with a Hi-Vis colloid mill head. After 15 min, 175 ml of 50% sodium hydroxide was added to adjust the pH to greater than 12 and the shearing continued for 45 min. The solids were washed two times with 200 l of de-ionized water in a 300 l vat before collecting the solids on a 25 μm filter bag. The pH of the solids was approximately 7. In the second stage treatment, the pH of the wet solids (volume amount 6 l), was adjusted to about 10 using 50% sodium hydroxide before adding 500 ml of 30% hydrogen peroxide and continued shearing for 45 min in a colloid mill (Premier Model Dispersator™). The slurry was stirred with mild agitation for 36 h and the wet solids were collected on a 25 μm filter bag. The corn fiber gel prepared before drying had a viscosity of 180 ± 20 P. The yield of the recovered dry product was 41%. The composition of the dried corn fiber gel was: moisture, 7.17%; total dietary fiber, 86.2%; protein, 1.28%; lipids, 0.20%, and minerals, 0.86%.

2.2.2. Oat cellulosic gel preparation

In a mixing tank, 270 kg fine ground oat hulls were mixed with 1460 kg water and heated to 90 °C. The pH was about 6.8 before adding 0.44 kg alpha-amylase (Taka-Therm L-340™). For the first stage treatment, the mixture was stirred for 15 min followed by addition of 48 kg of 50% sodium hydroxide and sheared in a colloid mill for 60 min. The resultant slurry was diluted with 3600 kg water at 95 °C before collecting the solids by centrifugation. The dilution and centrifugation steps were repeated until the pH of the solids was nearly nine. For the second stage treatment, the pH was adjusted to approximately 10 using 22 kg of 50% sodium hydroxide and 136 kg of 35% hydrogen peroxide added before shearing the mixture in a colloid mill for 60 min. The slurry was allowed to stand without agitation for 10 h before shearing again for 30 min. The slurry was centrifuged at about 50 °C to collect a white gel which was re-slurried with warm water and re-centrifugated until the gel's pH dropped to about eight. Drum drying was used to dry the gel. The yield of the recovered dry product was 37%. The oat fiber had a composition as follows: moisture, 8.20%; total dietary fiber, 84.2%; minerals, 6.14%; protein, 1.20%, and lipids, 0.26%.

2.3. Sample preparation

Samples for the rheological experiments were prepared by dispersing the appropriate cellulosic fiber gel (produced from corn, or oat hulls) in deionized water at a concentration of 8% by weight. The concentrations were not corrected for moisture in the solid material. The suspension was agitated using a Brinkman Industries Polytron homogenizer at speeds of 2000, 4000 or 7000 rpm. Some viscous heating occurred during the mixing process. The mixture was then heated to near boiling on a hot plate, cooled to room temperature, and used in the experiments. Fresh samples were made daily to ensure that the material had not undergone decomposition. Sample variations typically were within the range of ±10%. In this work, the samples are designated in accord with their botanical origin and mixing speeds, i.e. Corn 2k, Corn 4k, Oat 2k, and Oat 7k.

2.4. Rheological measurements

Rheological properties of the suspensions were measured using a Rheometrics ARES Series V controlled-strain rheometer (Rheometrics Scientific, Piscataway, NJ) operating under Rheometrics' Orchestrator™ Version 6.4.5 software. All the rheological studies were conducted using 25 mm diameter parallel plates at a gap of 2 mm. Both smooth surface and serrated plates were used to examine potential problems with sample slip. The temperature of the sample was controlled using a forced-air oven equipped with a mechanical chiller which enabled the chamber of the viscometer to be controlled to better than ± 0.1 °C. All the experiments reported herein were conducted at 23 °C and the data were inspected to ensure that all the measurements were performed within the torque range of the rheometer.

Strain sweep experiments were conducted at an applied frequency of 1 rad/s and at applied strains ranging from 0.01 to 100% to investigate the onset of nonlinear VE behavior. Stress relaxation experiments were conducted with applied strains ranging from 0.03 to 100% over 1000 s. Steady shear rate sweep experiments were performed with applied shear rates ranging from 0.001 to 10 or 100 s^{-1}, the experiments were terminated when applied shear rate reached a level which caused the sample to extrude from between the parallel plates. Start-up of steady-state shear experiments were conducted with applied shear rates of 0.001, 0.01, 0.1, and 1 s^{-1}. The shear rates were each applied for 600 s. Oscillatory shear flow experiments were performed with applied strains ranging from 0.1 to 20% over a frequency range of 0.1–100 rad/s.

The fits to the experimental data and calculations for the Wagner constitutive model predictions were performed using Mathsoft MathCad 6.0 and Waterloo Maple V software running on a 500 MHz Apple Macintosh G4 computer. Graphical presentations of the data and model predictions were generated using Wavemetrics Igor Pro 4.0 software.

2.5. Constitutive model

The constitutive equation used in this work is the Wagner model, which derives from the K-BKZ equation. The Wagner model may be expressed as (Bernstein, Kearsley, & Zapas, 1963; Wagner, 1976, 1978)

$$\underline{\underline{\tau}} = -\int_{-\infty}^{t} m(t-t')h(\mathrm{I}_B, \mathrm{II}_B)\underline{\underline{B}}(t')\mathrm{d}t' \quad (1)$$

where $\underline{\underline{\tau}}$ is the stress dyadic, $\underline{\underline{B}}(t')$ is the Finger strain dyadic which describes the strain history imparted to the material, $m(t-t')$ is the memory function, and $h(\mathrm{I}_B, \mathrm{II}_B)$ is the damping function which is expressed in terms of the first and second invariant of the Finger strain dyadic. In simple shear, the damping function becomes a function of the strain, γ. Implicit in the presentation of Eq. (1) is the assumption of strain-time factorability. The memory function in Eq. (1) may be expressed as a summation of exponentials

$$m(t-t') = -\frac{\partial G(t-t')}{\partial t} = \sum_{\mathrm{p}} \frac{G_{\mathrm{p}}}{\tau_{\mathrm{p}}} \mathrm{e}^{-(t-t')/\tau_{\mathrm{p}}} \quad (2)$$

where $G(t-t')$ is the stress relaxation modulus, and the set G_{p} and τ_{p} define the relaxation behavior of the material.

Application of Eq. (1) first requires that the relaxation function be determined from the linear VE regime. Once the linear VE range is determined, the damping function can then be calculated from the ratio of the nonlinear stress relaxation modulus, $G(\gamma, t-t')$, to the linear stress relaxation modulus, $G(t-t')$,

$$h(\gamma) = \frac{G(\gamma, t-t')}{G(t-t')} \quad (3)$$

Many different forms have been advanced for the damping function by Laun (1978), Soskey and Winter (1984) and Wagner (1976, 1978) to name the most widely used (Eqs. (4)–(6)). These equations may be expressed as

$$h(\gamma) = \mathrm{e}^{-K\gamma} \quad (4)$$

$$h(\gamma) = \frac{1}{1 + a\gamma^b} \quad (5)$$

$$h(\gamma) = K\mathrm{e}^{-a_1\gamma} + (1-K)\mathrm{e}^{-a_2\gamma} \quad (6)$$

where γ is the shear strain, and K, a, b, a_1, and a_2 are fitting parameters for the various formulations. For many synthetic polymeric materials the double exponential equation proposed by Laun has been used extensively to describe the nonlinear VE behavior at large strains. Once a damping function has been selected and the linear VE behavior of the material has been evaluated, the nonlinear behavior of the system can be predicted using Eq. (1).

3. Results and discussion

3.1. Evaluation of linear VE behavior

The effect of shear strain on the measured dynamic storage modulus, $G'(\omega, \gamma)$, at a frequency of 1 rad/s for each of the materials is illustrated in Fig. 1. For each of the suspensions, a region of linear VE behavior, i.e. $G'(\omega, \gamma)$ is independent of strain, is observed up to an applied strain, γ, of approximately 1%. At strains higher than 1%, $G'(\omega, \gamma)$ is observed to decrease with increasing strain indicating nonlinear VE behavior. Although the onset of nonlinear VE behavior appears not to be affected by the processing speed, the absolute modulus of the four materials is affected. For both corn and oats, the higher processing speeds produce a material with a higher value of $G'(\omega, \gamma)$ indicating the possible formation of a more densely entangled network.

The response of the Corn 2k suspension during stress relaxation experiments at various applied strains is illustrated in Fig. 2. The applied strains used were 0.03–100%. As was observed in the strain sweep experiments illustrated in Fig. 1, the suspension displays linear VE behavior for strains up to 1%. At strains higher than 1% the stress relaxation modulus, $G(t, \gamma)$, is observed to drop in magnitude with increasing applied strain. Similar behavior was observed for the other suspensions. The onset of nonlinear VE behavior does not appear to be a function of

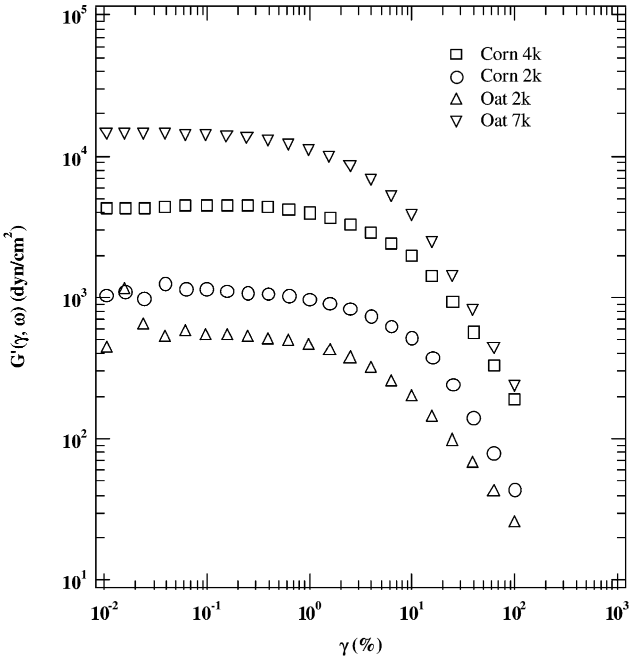


Fig. 1. Effect of applied strain on the oscillatory shear modulus for the various suspensions at 25 °C.

either the botanical type, or the applied processing conditions. Evidence of strain hardening behavior was not found for any of the materials over the applied strain range. For each of the suspensions, the stress relaxation data obtained in the linear VE regime was used to fit the memory function parameters, the results of which are summarized in Table 1.

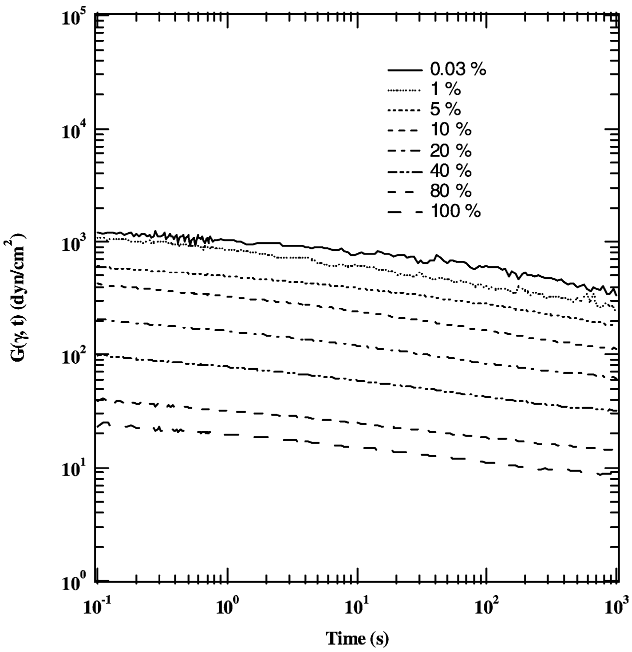


Fig. 2. Stress relaxation behavior of the Corn 2k suspension at 23 °C.

Table 1
Fitting parameters for Wagner model of cellulosic fiber gels

Material	τ_p	G_p	a	b
Con 2k	0.02 ± 0.001	812 ± 10	1.0 ± 0.1	0.272 ± 0.003
	0.278 ± 0.008	202 ± 10		
	3.87 ± 0.06	301 ± 20		
	54 ± 0.5	73 ± 6		
	748 ± 3	708 ± 80		
Corn 4k	0.02 ± 0.001	5427 ± 200	1.0 ± 0.1	0.272 ± 0.003
	0.299 ± 0.004	1422 ± 30		
	4.47 ± 0.02	1574 ± 80		
	66.9 ± 0.06	738 ± 10		
	1000 ± 0.5	2291 ± 90		
Oat 2k	0.01 ± 0.001	922 ± 30	1.0 ± 0.1	0.272 ± 0.003
	0.165 ± 0.002	771 ± 40		
	2.74 ± 0.02	1045 ± 20		
	45 ± 0.7	399 ± 10		
	748 ± 8	1542 ± 100		
Oat 7k	0.02 ± 0.001	19370 ± 800	1.13 ± 0.03	0.586 ± 0.004
	0.299 ± 0.003	5351 ± 60		
	4.48 ± 0.03	9458 ± 30		
	66 ± 0.7	2257 ± 90		
	1000 ± 1	21040 ± 200		

3.2. Evaluation of the damping function

The damping function in the Wagner model can be determined from the ratio of the nonlinear stress relaxation modulus at a specific strain level to the linear stress relaxation modulus as described earlier. The damping function for each of the four materials is displayed in Fig. 3. From Fig. 3, it is evident that the nonlinear VE behavior of the two products produced from corn at 2000 and 4000 rpms, respectively, and the product produced from oats at a processing speed of

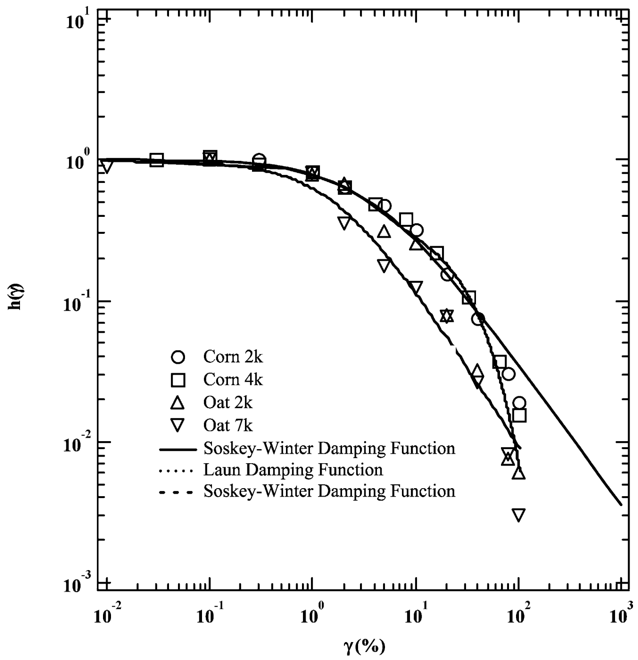


Fig. 3. Damping function fits to the Corn 2k, Corn 4k, Oat 2k, and Oat 7k suspensions at 23 °C.

2000 rpm all can be described by a single damping function. The nonlinear VE behavior of the material produced from oats at 7000 rpm displays a different profile. The Wagner, Soskey-Winter, and Laun damping functions (Laun, 1978; Soskey & Winter, 1984; Wagner, 1976, 1978) were all evaluated for each of the materials. The Wagner damping function could not accurately describe the high-strain behavior of any of the materials (data not displayed). The Soskey-Winter damping function could describe the majority of the strain-dependence of the material, but also failed to describe the high-strain region accurately. The Laun damping function provided the most accurate description of the nonlinear VE behavior of the materials, however, it led to a prediction in the change of the shear-thinning behavior of the materials that was not observed experimentally (as discussed below). For the majority of the predictions discussed in this work, the Soskey-Winter damping function was utilized. The fitted parameters for the Soskey-Winter damping function are summarized in Table 1 for each of the suspensions.

3.3. Viability of the assumption of strain-time separability

As mentioned earlier, an essential aspect of the Wagner model is the assumption of time-strain separability. Time-strain separability in rheological data may be examined by plots of $G(\gamma,t)/h(\gamma)$ versus the logarithm of time for each applied strain. (Osaki, Nishizawa, & Karata, 1982). Over the strain range that time-strain separability holds, the graphs should collapse to a single curve. A plot of $G(\gamma,t)/h(\gamma)$ versus $\log(t)$ is illustrated in Fig. 4 for the Oat 2k sample at strains of 1, 10, 40, and 100%. From the data displayed in the figure it is evident that time-strain separability is valid

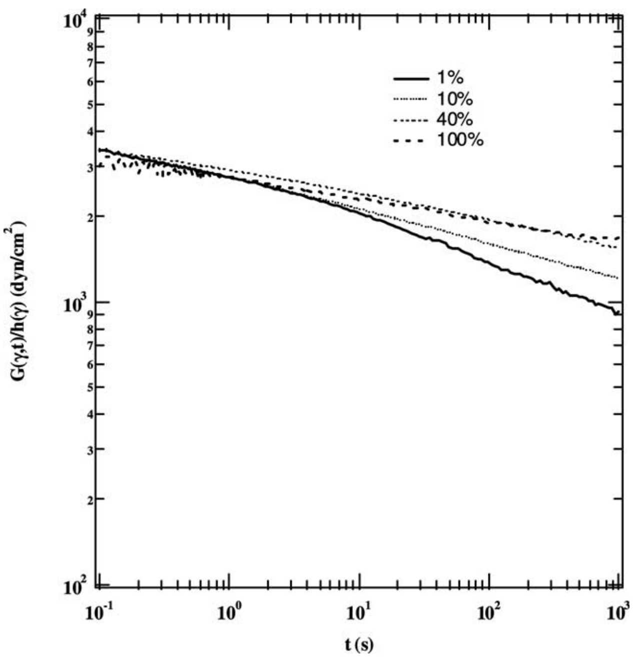


Fig. 4. Test of strain-time separability for the Oat 2k suspension at 23 °C.

for the range of applied strains used in this investigation. Similar results were found for the other samples.

3.4. Prediction of nonlinear rheological behavior

3.4.1. Steady-shear rate sweep

The results of a steady-shear rate sweep experiments on the Corn 2k, Corn 4k, Oat 2k, and Oat 7k suspensions are illustrated in Fig. 5. Each of the suspensions exhibits shear-thinning behaviors across the entire shear rate range studied without any evidence of strain hardening behavior. Due to torque limitations of the rheometer transducer, measurements of the zero-shear viscosity for the suspensions could not be made. For each of the suspensions, the drop in viscosity with decreasing shear rate observed at the lowest shear rates could possibly be due to the destruction of weak structures formed in these system, although more work needs to be performed to verify this assumption. Shear-thinning behavior has been found for other beta-glucan containing materials (Carriere & Inglett, 1998, 1999; Doublier & Wood, 1995).

For steady shear rate sweep experiments the Wagner model at any shear rate may be rewritten as

$$\eta(\dot{\gamma}) = \int_0^{t_{\mathrm{meas}}} G(s)\left[s\frac{\partial h(s)}{\partial s} + h(s)\right]\mathrm{d}s \tag{7}$$

where $\eta(\dot{\gamma})$ is the steady shear viscosity calculated at a shear rate of $\dot{\gamma}$, and t_{meas} is the time of measurement at each shear rate, which for these experiments was 12 s. For linear VE behavior, with $h(s) = 1$, Eq. (7) yields the zero-shear viscosity. The prediction of the steady shear rate behavior of each of the suspensions is illustrated in Fig. 5. Using the Laun damping function, Eq. (6), the model correctly predicts the observed shear-thinning behavior, however the model predicts a change in the shear-thinning behavior for the Corn 2k, Corn 4k, and Oat 2k suspensions at a shear rate of 0.1 s^{-1}. For Oat 7k the model, using the Laun damping function, predicts a change in the shear-thinning behavior of the suspension at shear rate of 0.01 s^{-1}. Neither of these behaviors are observed experimentally. The Soskey-Winter damping function also predicts observed shear-thinning behavior for each of the suspensions. The use of the Soskey-Winter damping function also provided a more accurate prediction of the magnitude of the shear viscosity across the shear rate range studied than did the Laun damping function. The model using the Soskey-Winter damping function did not predict the change in the shear-thinning behavior, which was predicted using the Laun damping function, but was not observed experimentally.

3.4.2. Successive start-up of steady-state shear

The responses of the four suspensions to the start-up of steady-state shear flow are illustrated in Fig. 6. For the Corn 2k suspension, the shear stress growth function, $\eta^{+}(\dot{\gamma},t)$, displays slight stress overshoot behavior at shear rate of 0.1 and 1 s^{-1}. At all shear rates, $\eta^{+}(\dot{\gamma},t)$ quickly obtains

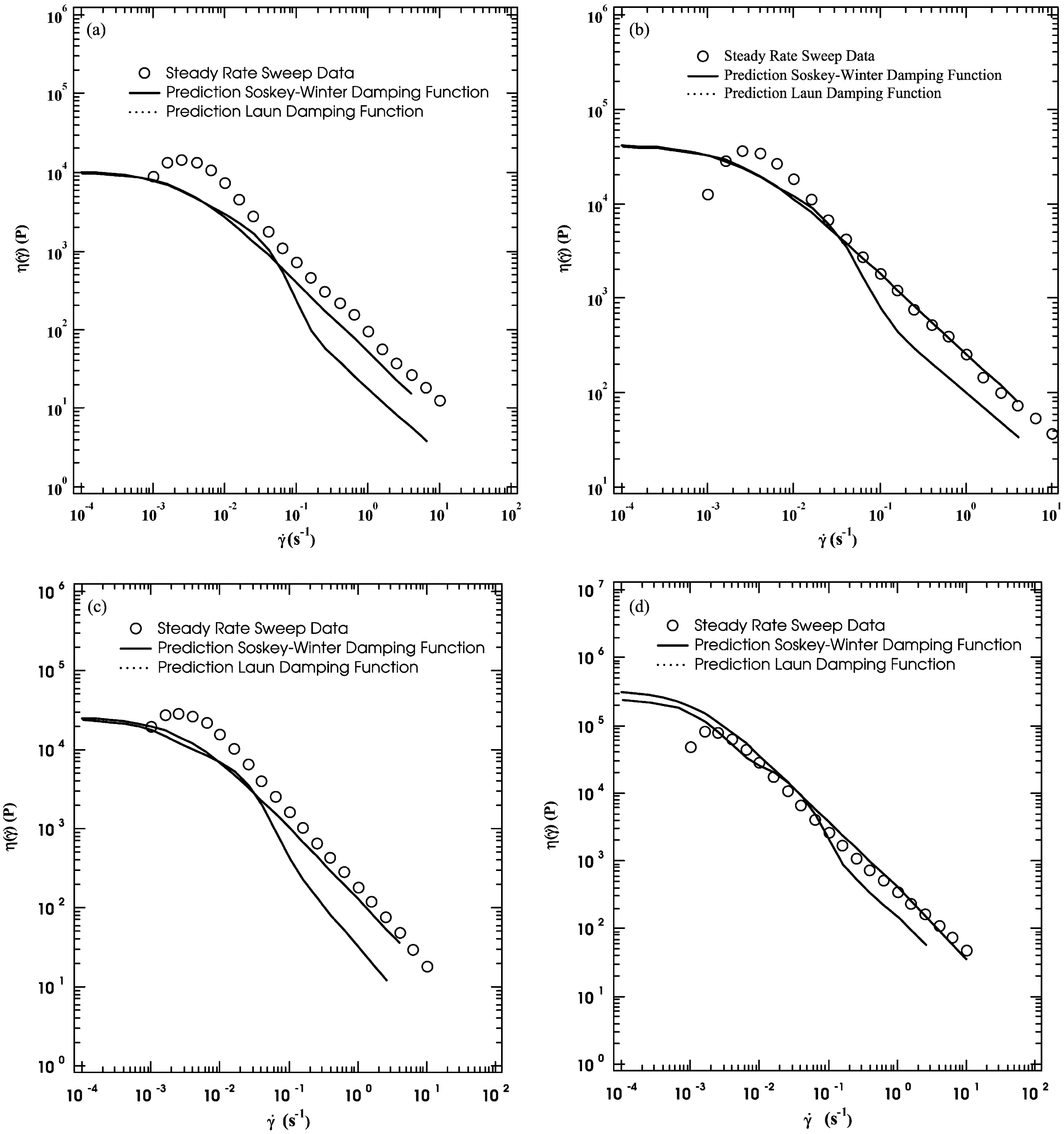


Fig. 5. Steady-state rate sweep behavior of the (a) Corn 2k; (b) Corn 4k; (c) Oat 2k; and (d) Oat 7k suspensions at 23 °C. Predictions of the rheological behavior of the suspensions using the Wagner model are displayed as solid (Soskey-Winter damping function) or dashed (laun damping function) lines, respectively.

a steady plateau value within 100 s of the application of the shear field. For the Corn 4k suspension, $\eta^{+}(\dot{\gamma}, t)$ exhibited a slightly stress overshoot only at the highest applied shear rate, 1 s^{-1}. At the lower shear rates, a stable plateau was reached within 100 s of the application of the shear field. For the Oat 2k and 7k suspensions, only the Oat 7k suspension, after the application of 1 s^{-1} shear field, displayed any stress overshoot. At all of the applied shear rates a steady plateau value was reached. None of the samples displayed any thixotropic behavior.

For the start-up of steady-state shear experiment the Wagner model may be rewritten as

$$\eta^{+}(\dot{\gamma}, t) = \int_{0}^{t} G(s)\left[s\frac{\partial h(s)}{\partial s} + h(s)\right] \mathrm{d}s \tag{8}$$

where $G(s)$, and $h(s)$ are defined in Eqs. (2) and (6), respectively. The prediction of the Wagner model for linear VE behavior may be calculated using Eq. (8) with $h(s) = 1$. The prediction using the Wagner model for each of the suspensions during the start-up of stead-state shear is

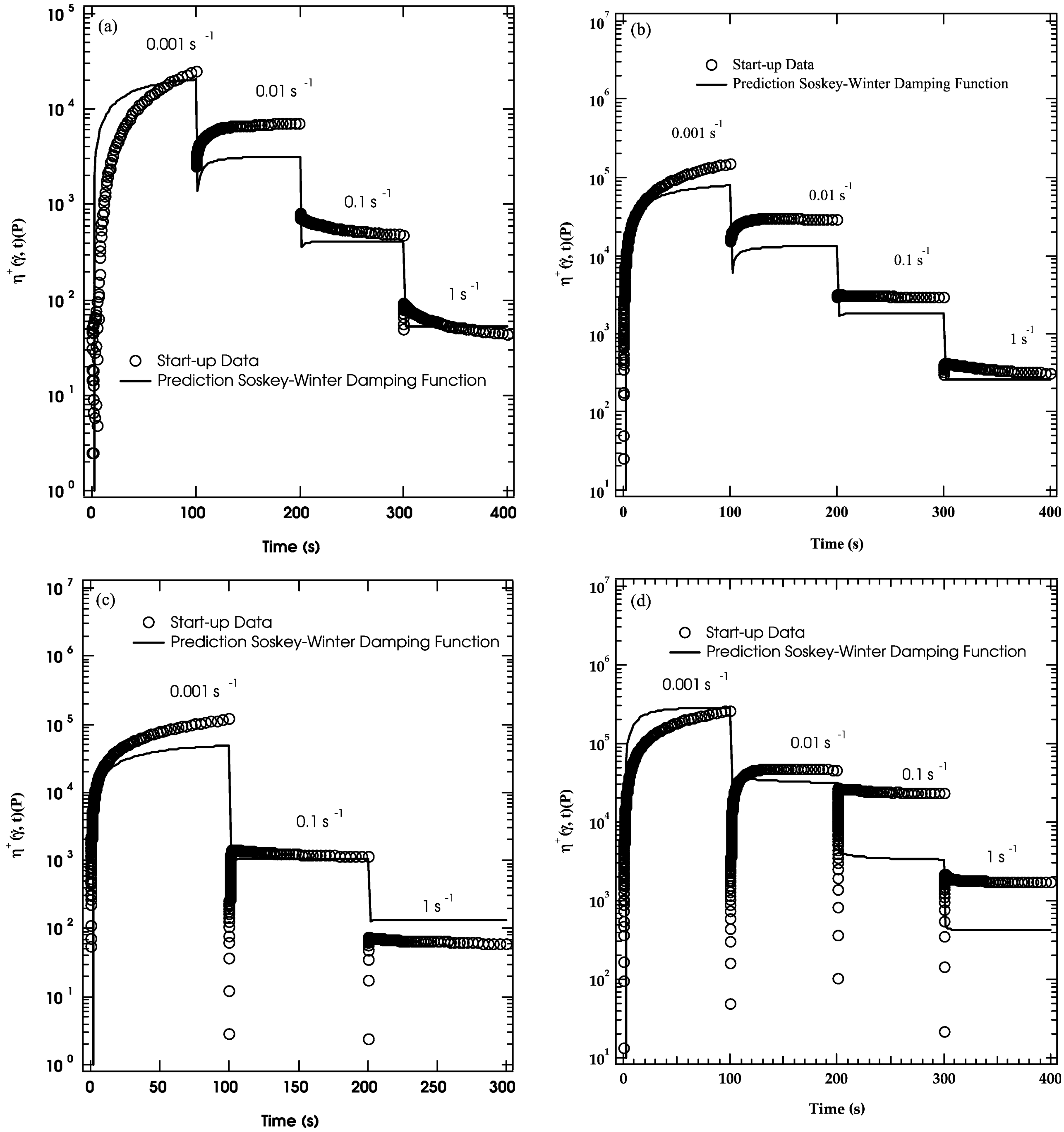
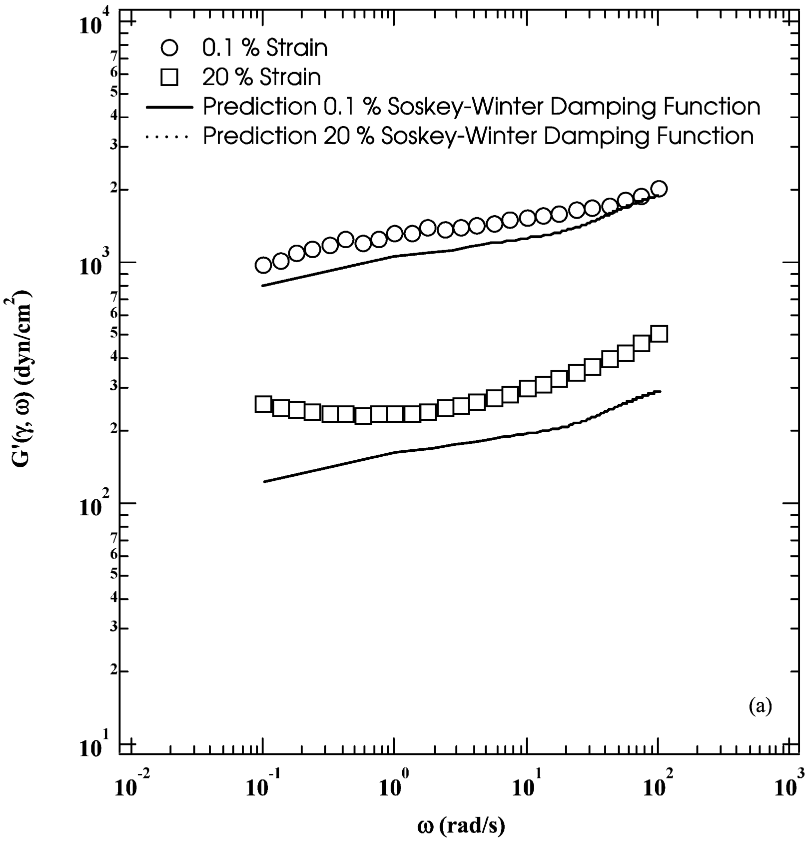


Fig. 6. Start-up of steady-state shear response of the (a) Corn 2k, (b) Corn 4k, (c) Oat 2k, and (d) Oat 7k suspensions at 23 °C. Predictions of the rheological behavior of the suspensions using the Wagner model are displayed as solid lines.

illustrated in Fig. 6. For each of the suspensions the Wagner model provides an accurate description of the response of the material to the onset of steady-state shear flow. The model does not predict unobserved stress overshoots for any of the suspensions at the various shear rates studied.

3.4.3. Oscillatory shear flow

The results of oscillatory shear flow experiments on Corn 2k, Corn 4k, Oat 2k, and Oat 7k suspensions at applied strains of 0.1 and 20% are illustrated in Fig. 7. For each of the suspensions, $G'(\gamma, \omega)$ displays a very slight dependence on the oscillatory frequency, ω, indicative of the gel-like behavior of the corn, or oat suspensions. The character of the curves in both the linear VE regime (0.1% strain) and the nonlinear VE regime (20% strain) are similar in overall character with the higher strain level causing a decrease in the absolute value of $G'(\gamma, \omega)$.



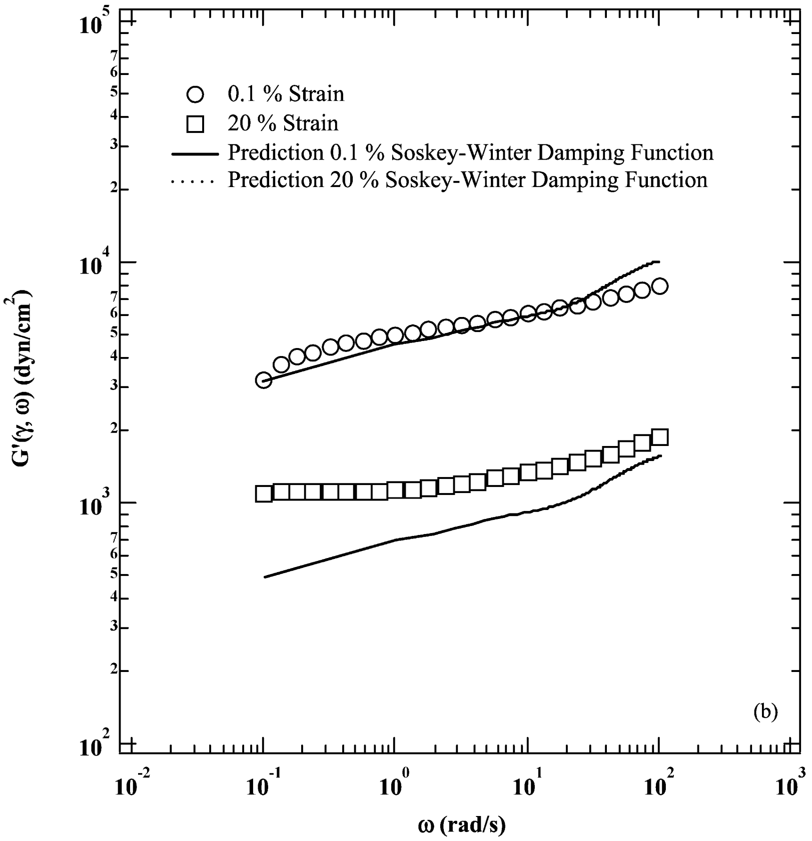
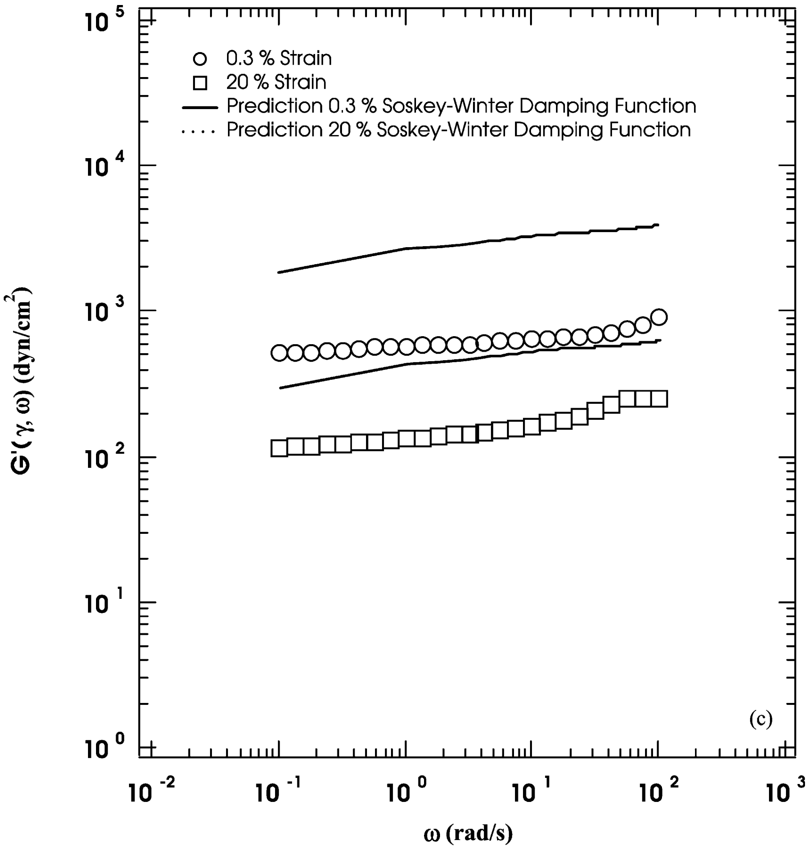


Fig. 7. Oscillatory shear flow response of the (a) Corn 2k, (b) Corn 4k, (c) Oat 2k, and (d) Oat 7k suspensions at 23 °C. Predictions of the rheological behavior of the suspensions using the Wagner model are displayed as solid lines.



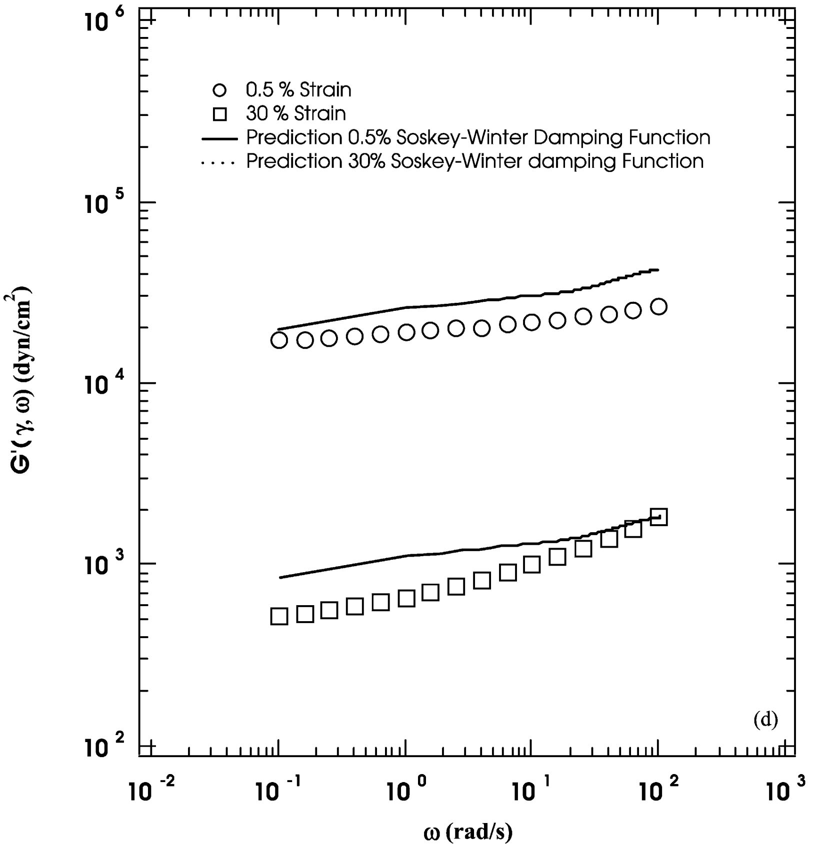


Fig. 7 (*continued*)

For the oscillatory shear flow experiment the Wagner model may be recast as

$$\sigma'(\gamma,\omega) + j\sigma''(\gamma,\omega) = -\int_{-\infty}^{t} m(t-t')h(\gamma)\gamma_0 e^{j\omega t'}\,dt' \qquad (9)$$

where $\sigma'(\gamma,\omega)$, and $\sigma''(\gamma,\omega)$ are the real and imaginary components of the oscillatory shear stress, ω is the angular frequency of the deformation, γ_0 is the peak amplitude of the strain, and $j=\sqrt{-1}$. The storage and loss moduli can be calculated from the real and imaginary components of the stress using $G'(\gamma,\omega)=\sigma'(\gamma,\omega)/\gamma_0$, and $G''(\gamma,\omega)=\sigma''(\gamma,\omega)/\gamma_0$, respectively.

The predictions of the Wagner model for the various suspensions under oscillatory shear flow are illustrated in Fig. 7 as solid (0.1% strain), or dashed (20% strain) lines. For each of the suspensions the predictions of the Wagner model provide a reasonable description of the observed frequency response of $G'(\gamma,\omega)$. In addition, with the exception of the Oat 2k sample, the model also provides a suitable prediction of the absolute value of $G'(\gamma,\omega)$ at both 0.1 and 20% strains.

4. Conclusions

The nonlinear VE behavior of cellulosic fiber gel suspensions produced from corn and oat hulls were characterized. The gel suspensions were found to exhibit shear-thinning behavior with nonlinear VE behavior evidenced at strains above 1%. The linear and nonlinear VE performance of the suspensions was analyzed using a Wagner integral constitutive model. The damping function used in the model was evaluated from stress relaxation data with the Soskey-Winter formulation being found to provide the best description of the nonlinear behavior of these suspensions. The Wagner model was used to predict the performance of the various suspensions under difference shear deformations including steady state shear, start-up and oscillatory shear, and oscillatory shear. The Wagner model was found to provide an adequate description of the nonlinear VE behavior of the suspensions produced from corn, or oat hulls.

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References

AACC (1983). *Approved methods of the American association of cereal chemists*. St Paul, MN: American Association of Cereal Chemists.

AOAC (1990). *Official methods of the American association of analytical chemists*. Washington, DC: American Association of Analytical Chemists.

Bernstein, B., Kearsley, E. A., & Zapas, L. J. (1963). A theory of stress relaxation with finite strain. *Transaction Society of Rheology*, *7*, 391–410.

Carriere, C. J., & Inglett, G. E. (1998). Solution viscoelastic properties of OATRIM-10 and cooked oat bran. *Cereal Chemistry*, *75*, 354–359.

Carriere, C. J., & Inglett, G. E. (1999). Nonlinear viscoelastic solution properties of oat-based b-glucan/amylodextrin blends. *Carbohydrate Polymer*, *40*, 9–16.

Doublier, J.-L., & Wood, P. J. (1995). Rheological properties of aqueous solutions of (1-3)(1-4)-beta-D-glucan from oats (*Avena sativa* L.). *Cereal Chemistry*, *72*, 335–340.

Lapasin, R., & Pricl, S. (1995). *Rheology of industrial polysaccharides*. UK: Chapman, pp. 419–423.

Lapasin, R., Pricl, S., & Tracanneli, P. (1992). Different behavior of concentrated polysaccharide systems in large-amplitude oscillatory fields. *Rheology Acta*, *31*, 374–380.

Laun, H. M. (1978). Description of the nonlinear shear behavior of a low density polyethylene by means of an experimentally determined strain dependent memory function. *Rheology Acta*, *17*, 1–15.

Matsumoto, T., Hitomi, C., & Onogi, S. (1975). Rheological properties of disperse systems of spherical particles in polystyrene solutions at long time scales. *Transaction Society of Rheology*, *19*, 541–555.

Osaki, K., Nishizawa, K., & Kurata, M. (1982). Material time constant characterizing the nonlinear viscoelasticity of entangled polymer systems. *Macromolecules*, *15*, 1068–1071.

Russel, W. B. (1980). Review of the role of colloidal forces in the rheology of suspensions. *Journal of Rheology*, *24*, 287–314.

Russel, W. B., Saville, D. A., & Scholwater, W. R. (1989). *Colloid dispersion*. UK: Cambridge.

Simhambhatla, M., & Leonov, A. I. (1995). On the rheological modeling of filled polymers with particle–matrix interactions. *Rheology Acta*, *34*, 329–338.

Soskey, P. R., & Winter, H. H. (1984). Large step strain experiments with parallel-disk rotational rheometers. *Journal of Rheology*, *28*, 625–645.

Wagner, M. H. (1976). Analysis of time-dependent non-linear stress-growth data for shear and elongational flow of low-density branched polyethylene melt. *Rheology Acta*, *15*, 136–142.

Wagner, M. H. (1978). A constitutive analysis of uniaxial elongational flow data of a low-density polyethylene melt. *Journal of Non-Newtonian Fluid Mechanics*, *4*, 39–55.

Watanabe, H., Yao, M.-L., Osaki, K., Shikata, T., Niwa, H., & Morishima, Y. (1996). Nonlinear rheological behavior of a concentrated spherical silica suspension. *Rheology Acta*, *35*, 433–445.

Watanabe, H., Yao, M.-L., Osaki, K., Shikata, T., Niwa, H., & Morishima, Y. (1997). Nonlinear rheology of a concentrated spherical silica suspension 2. Role of strain in shear-thickening. *Rheology Acta*, *36*, 524–533.